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DEFECTS IN ALUMINUM QUENCHED FROM THE LIQUID STATE

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DEFECTS IN ALUMINUM QUENCHED FROM THE LIQUID STATE

by

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Approved by Pol Duwez
Professor of Materials Science

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ABSTRACT

High purity aluminum was quenched from the liquid state and specimens were examined by transmission electron microscopy. Very high densities of defects in the form of perfect loops, imperfect loops, and small black spots were observed. The vacancy concentration, as deduced from the number and size of defects, increase with increasing temperature at a much slower rate in the liquid than in the solid. Both the vacancy formation energy and the entropy factor appear to be considerably reduced above the melting point. Also, a discontinuity in the vacancy concentration is observed at the melting point.

1. INTRODUCTION

Previous experiments on the quenching-in of vacancies in metals have been limited to solid state quenching with cooling rates of the order of fifty thousand degrees per second. It is now well known that in quenched metals, vacancies condense out in various dislocation configurations, namely, perfect loops, imperfect loops, or tetrahedra, depending upon stacking fault energy, purity and vacancy supersaturation (see reviews in Refs. 1 and 2). The quenching-in of vacancies in high purity solid aluminum has been studied previously by resistivity(4,5), transmission electron microscopy(6-8), and simultaneous x-ray and dilatometry(9). The vacancy concentration can be expressed as $c = A \exp-(Q_f/kT)$ where, for aluminum, $A = 8$ and $Q_f = 0.76$ eV. At the melting point of aluminum (933°K), the vacancy concentration is 6×10^{-4}.

The method of rapid quenching from the melt, described by Duwez and Willens(3), offers the possibility of investigating the quenching-in of vacancies from the liquid state. It has been estimated that the cooling rates achieved by this quenching technique are of the order of one or two million degrees per second. The experiments described in this paper are carried out on quenched liquid aluminum. Both the variations of vacancy concentration with quenching temperature and the type of vacancy defects that were formed have been investigated.

2. EXPERIMENTAL PROCEDURE

The aluminum used in this investigation had a purity of 99.996%, magnesium being the predominant impurity (30 ppm). The foils produced by this quenching technique were non-uniform in thickness, the average thickness being of the order of several microns. However, there were regions within the foil which were thin enough to be viewed in transmission electron microscopy without any further thinning being necessary[10]. Only these regions were examined to determine the vacancy concentrations. In most cases, the foil was observed immediately after quenching without aging at elevated temperatures. Some foils were aged for several minutes between 100°C and 140°C. No difference in structure between the as-quenched foil and the aged foils was noticed except for some loop growth. The high concentration of vacancies which were retained by the quench resulted in the formation of Frank-sessile loops, perfect loops, and small dark spots which may be very small loops or vacancy clusters. The vacancy concentration was determined from the size and density of loops using the formula $c = \pi r^2 bn/t$, where $\underline{n}$ is the number of loops per cm^2, $\underline{r}$ the loop radius, $\underline{b}$ the Burgess vector ($a/3\langle 111\rangle$ for Frank loops, $a/2\langle 110\rangle$ for perfect loops) and $\underline{t}$ the foil thickness. For the case of spherical clusters with radius $\underline{r}$, this formula would underestimate the vacancy concentration by a factor of $4r/3b$. The actual foil thickness was of the order of 3×10^{-5} cm, however, a value of 10^{-5} cm was adopted for the calculations in view of the fact that vacancy denudation occurs at both the top and bottom surfaces of the foil.

3. RESULTS

Typical electron micrographs from foils quenched from various temperatures above the melting point are shown in Figs. 1 to 6. Quenches from below 1200°C produce large numbers of loops or clusters.

Figure 1. Defect structure in aluminum quenched from 1165°C showing high density of loops and black spots.

Figure 2. Defect structure in aluminum quenched from 725°C. There is a narrow denuded zone between 500 and 1000 A wide, next to grain boundaries.

Figure 3. Defect structure in aluminum quenched from 765°C. A zig zag dislocation has produced a loop-free area A.

Figure 4. Loops and black spots in a (111) area after quenching from 1165°C. Operating reflection $(2\bar{2}0)$. Notice absence of loops in the (111) plane showing they are all of the Frank-sessile kind (b = a/3 [111]).

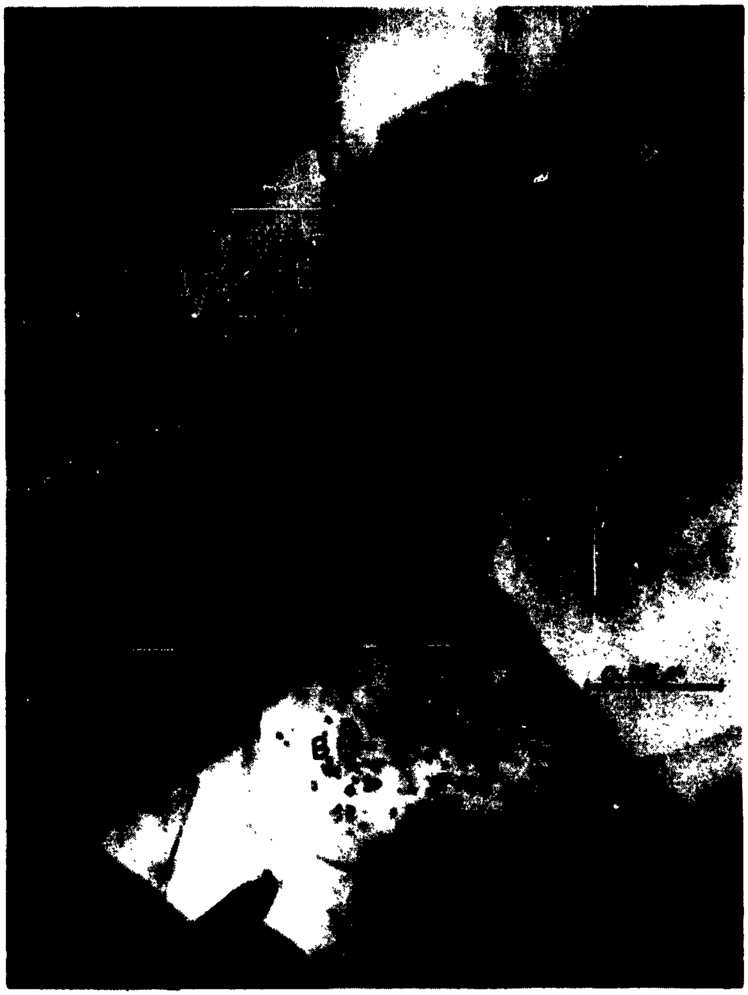

Figure 5. Small grain size in Al quenched from 900°C. By tilting the specimen, the loops in region A can be brought into contrast. Large perfect diamond-shaped loops are visible at B.

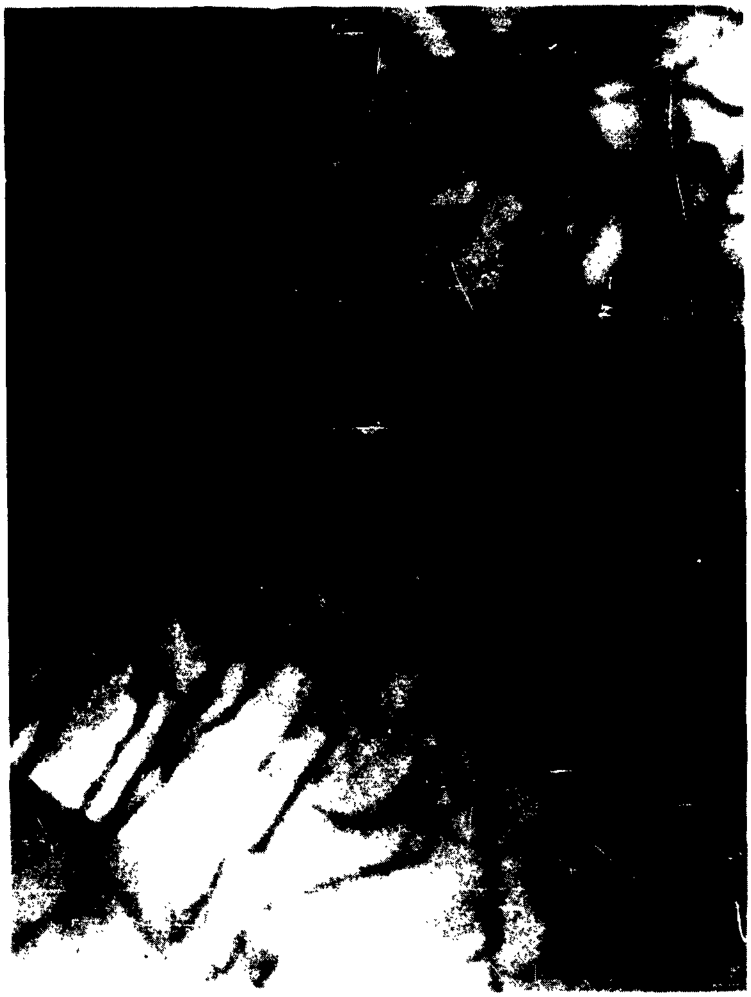

Figure 6. Aluminum quenched from 1260°C. Notice the absence of loops and the high density of dislocations making sub-boundaries.

At higher temperatures few loops are observed but the density of dislocations is very large (Fig. 6). Below 1200°C most of the dislocations appear to be in the form of loops except as shown at A in Fig. 3 where a zig zag dislocation line exists in a loop-free area. Apparently many dislocations are generated by quenching from temperatures greater than 1200°C and these effectively sweep up most of the retained vacancies. In addition, the quenching efficiency is probably reduced with increasing temperature of the melt due to the thermal capacity of the sample. Thus some vacancies will have time to escape from the thin regions of the foil during cooling. As shown in Figs. 1 and 2 very high densities of defects are observed after quenching from below 1200°C. The grain size is very small (1/4 to 1μ) and the grains have nearly equilibrium shapes (Fig. 5). Another interesting feature is that the width of the vacancy denuded zone is between 500 and 1500 Å which is much less than that observed in aluminum quenched from below the melting point (1,4). This fact and the observed high densities of defects indicate that numerous vacancies have been quenched-in.

Perfect and imperfect dislocation loops have been resolved as well as small spherical black spots (Figs. 3 and 4) which could be small loops or vacancy clusters. These three types of defects are observed in specimens quenched from below 1200°C. Figure 4 is an example of an area in (111) orientation. Only three orientations of loops are visible corresponding to the traces of $(\bar{1}11)$ $(1\bar{1}1)$ and $(11\bar{1})$ planes with the foil surface. Loops in the plane of the foil are not visible, indicating that the Burgers vector must be normal to the foil surface. This must mean that the loops are of the Frank kind since perfect loops would have all four possible orientations visible in the (111) orientation. Most of the very small loops do appear to be Frank loops, but larger, perfect loops, many of which are diamond-shaped, are also observed (for instance at B, Fig. 5).

Table I gives the number of defects per cm^3 and the average vacancy concentration calculated on the basis of perfect loop defects. These results are probably on the low side because 1/ not all of the vacancies may have condensed to the loops, 2/ not all loops may be visible because of contrast conditions (Fig. 5) and, 3/ many of the defects may be spherical clusters and the concentration calculations, which assume loops, would underestimate the concentration.

TABLE I

Quenching Temperature (°C)	Treatment	Loop radius (A)	Number of Loops per cm^3	Average Vacancy Concentration $C \times 10^3$
725	As Cast	100	1.3×10^{16}	1.04
820	2 Min. at 136°C	250-625	1.6×10^{15}	1.34
1030	As Cast	100	1.5×10^{16}	1.29
1165	As Cast	110	1.4×10^{16}	1.60

A plot of ln c against reciprocal temperature is shown in Fig. 7. It can be seen that there is a sharp change in slope and a discontinuity in vacancy concentration at the melting point. The equation of the line, representing quenches from the liquid, is $c = 4 \times 10^{-3} \exp-(0.11/kT)$.

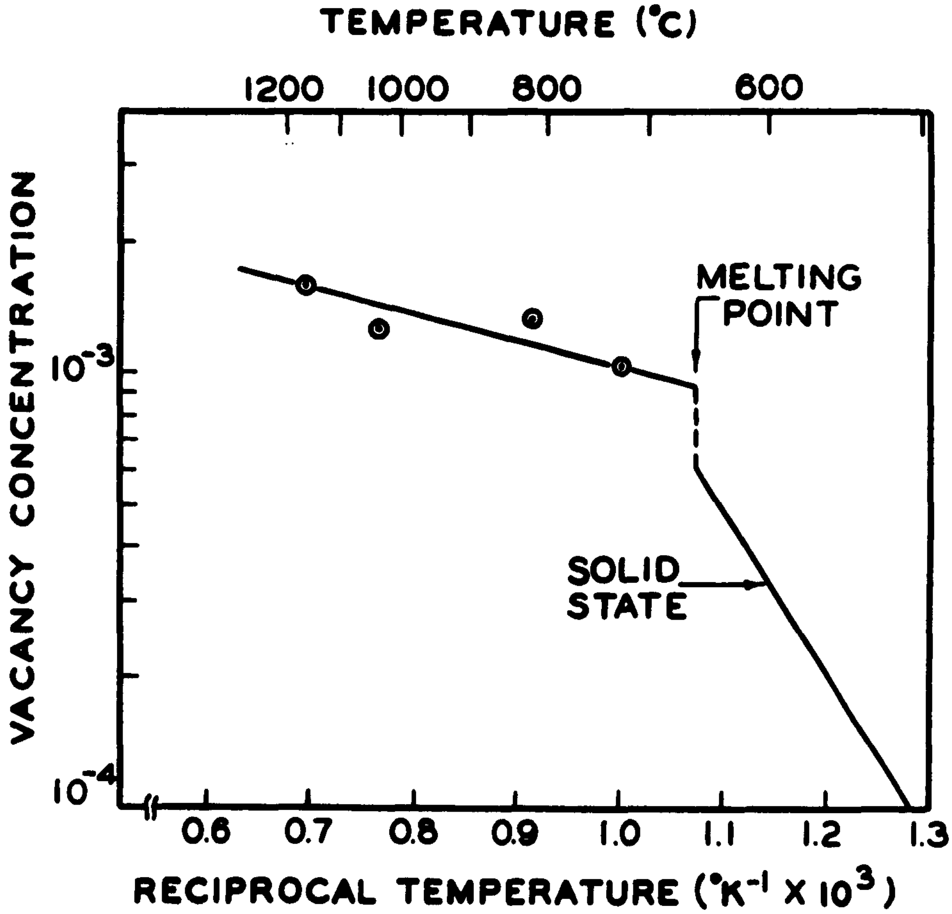

Figure 7. Relationship between vacancy concentration and reciprocal temperature. The solid state line is taken from the data of References 4 and 9.

DISCUSSION

The very high and uniform densities of defects observed in these experiments indicate that very large supersaturations of vacancies are retained by rapid quenching from the liquid state. The appearance of three kinds of defects, namely, perfect loops, imperfect loops, and small black spots, is indicative of various stages in the annihilation of vacancies depending upon local conditions of vacancy supersaturation and quenching stresses. Another possibility is that the defects may form at the solid-liquid interface[15]. Previous calculations[16,17] show that stable vacancy clusters or loops trapped behind the interface would not diffuse back to the liquid due to the high interfacial velocity (estimated to be 10 cm/sec.). These calculations are slightly in error because no change in the vacancy formation energy between the liquid and solid states and no discontinuity in equilibrium vacancy concentration are assumed.

The increase in vacancy concentration at the melting point contributes to the entropy of melting. Assuming a random two-component system, the increase in entropy on melting due to a change in vacancy concentration is[11]

$$\frac{\Delta S}{Nk} = \left[c_1 \ell n\, c_1 - c_2 \ell n\, c_2 + (1-c_1) \ell n\, (1-c_1) - (1-c_2) \ell n\, (1-c_2)\right] \quad ,$$

where c_1 is the vacancy concentration in the solid and c_2 the vacancy concentration in the liquid. Using $c_1 = 6 \times 10^{-4}$ and $c_2 = 1 \times 10^{-3}$ at the melting point, the entropy change is $2.9\ Nk \times 10^{-3}$. The total entropy change on melting, as deduced from the heat of fusion, is 1.4 Nk for aluminum. Therefore, the entropy increase associated with the change in vacancy concentration is very small. The largest contribution to the entropy change is probably configurational entropy, since there is evidence that the vibrational frequencies, the only other source of entropy associated with melting, is not appreciably altered[12,13,14].

Perhaps the most interesting results obtained in this investigation is that within the experimental limits of the electron microscopy technique, the vacancy concentration is relatively insensitive to temperatures above the melting point. The entropy factor and the formation energy of a vacancy are both smaller in the liquid than in the solid. The ratio is about three orders of magnitude in the entropy factor and about a factor of seven in the formation energy.

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